[Second Edition.]

PATENT SPECIFICATION.

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Cellulose.

I, HENRY DREYFUS, a British subject, of Celanese House, 22 & 23, Hanover Square, London, W.1, do hereby declare the nature of this invention to be as follows :—

This invention is concerned with improvements in the treatment of cellulosic materials and particularly in the purification of wood and other cellulosic materials in order to render them suitable for industrial purposes.

As is well-known, wood and other cellulosic materials in their natural state contain a number of other constituents, particularly lignin and pentosans and other hemi-celluloses, which must be removed before a cellulose is obtained which is sufficiently pure for most of the industrial purposes for which it is required, for example for the production of paper, viscose, nitrocellulose, cellulose acetate and other cellulose derivatives. Various methods are known for the treatment of crude cellulosic materials, the most important of these being the sulphite, soda, and sulphate processes. These methods give the well-known chemical wood pulps which in general require further treatments to obtain the purified cellulose of good colour containing a high percentage of alpha-cellulose which is employed in industry.

The present invention is concerned with a new method for the purification of wood and other cellulosic materials, for example straw, which is based on the use of oxygen, particularly in the form of hydrogen peroxide. This treatment may be carried out with an aqueous solution of hydrogen peroxide but it has been found that the reaction proceeds more satisfactorily and more rapidly if a medium containing an organic acid, particularly acetic acid or other lower fatty acid, is used.

The process is applicable to the treatment of all types of wood, both of a deciduous and non-deciduous character. For example the wood treated may be ash, oak, elm, poplar, birch, beech, larch, pine, spruce or fir. Preferably it is treated in a finely divided state, for instance in the form of sawdust or small chips. The hydrogen peroxide treatment may be assisted and the amount of hydrogen peroxide necessary reduced by boiling the cellulosic material with dilute alkali, for example 1% caustic soda solution prior to treating it with hydrogen peroxide. Boiling may, for example, be carried out for about an hour.

As indicated above, while a simple aqueous solution of hydrogen peroxide may be employed, the treatment is preferably effected with a solution of peroxide in an organic acid. Acetic acid is preferably used, though other organic acids, particularly lower fatty acids for example butyric or propionic acid, may also be employed. Acetic acid in a concentration of 25, 50 or 75% or more may be used, a concentration of about 40—60% being usually found most satisfactory. The rate of liquid to cellulosic material may e.g. be 10, 15 or 20 to 1. The amount of hydrogen peroxide necessary will depend to some extent on the nature of the wood or other cellulosic material but proportions of between 70 and 100 or 120% of the weight of the material are usually required. The reaction temperature is usually between about 40 and 70° C. and the time 4—6 hours.

It has also been discovered that the action of the hydrogen peroxide on the cellulosic materials may be assisted by the use of catalysts, which are preferably employed in conjunction with the acetic acid or other organic acid. Manganese acetate has been found to give good results and may be employed in an amount equal, for example, to 5, 10 or 15% of the weight of the materials. Other acetates which may be used are those of cobalt, nickel, iron, chromium, and aluminium. Metal salts of other organic acids may also be used. Ammonia also has been found to assist the action of the hydrogen peroxide and the treatment may be carried out with a solution of hydrogen peroxide in ammonia.

The principal effect of the treatment with hydrogen peroxide is to oxidise the ligneous constituents and render them soluble in dilute alkali. After the hydrogen peroxide treatment is completed, therefore, the cellulosic material may be

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boiled for a short time with a dilute solution of sodium hydroxide, for example a ½ or 1% solution, and then thoroughly washed. It may then be treated at ordinary temperature with a mercerizing solution of sodium hydroxide containing 9 to 15% of sodium hydroxide in order to remove hemi-celluloses, and this treatment may, if required, be repeated several times. In this manner a cellulose having a high alpha-cellulose content and substantially free from lignin, pentosans and other impurities may be produced.

The following Example is given to illustrate the invention:—

EXAMPLE.

One part of elm sawdust is boiled for about an hour with a 1% solution of sodium hydroxide, and then, after washing, is immersed in 12 parts of 45% acetic acid containing 0.8 part of hydrogen peroxide and 0.1 part of manganese acetate. It is heated in this solution for about 4 hours at 70° C. and, after separation from the liquor, boiled for 15 to 30 minutes with ½% solution of sodium hydroxide. Finally, it is mercerized for ½ hour with 8 parts of a 12% solution of sodium hydroxide, and the treatment repeated until the pentosan content has been reduced to a low figure. The wood is then washed, and may be employed, for the production of cellulose derivatives, for paper or other purposes.

The invention has been described above in relation to the use of hydrogen peroxide, which has been found to be the most suitable oxidising agent. Other sources of oxygen may, however, be employed, for example, sodium peroxide, oxygen alone or even air, either alone or in conjunction with small amounts of hydrogen peroxide. Preferably such other sources are also used with dilute acids containing manganese acetate or other catalyst.

Dated this 10th day of March, 1942.
STEPHENS & ALLEN,
Chartered Patent Agents.
Wykeham House,
Gordon Avenue, Stanmore, Middlesex.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Cellulose.

I, HENRY DREYFUS, a British subject, of Celanese House, 22 & 23, Hanover Square, London W.1, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of cellulose from wood and other cellulose-containing materials.

As is well known, wood and other cellulose-containing materials in their natural state contain a number of other constituents, particularly lignin and pentosans and other hemi-celluloses, which must be removed before a cellulose is obtained which is sufficiently pure for most of the industrial purposes for which cellulose is required, for example, for the production of paper, viscose, nitro-cellulose, cellulose acetate and other cellulose derivatives. Various methods are known for the treatment of cellulosic materials, the most important of these being sulphite, soda and sulphate processes. These methods give the well known chemical wood pulps which in general require further treatments to obtain a cellulose of good colour containing a high percentage of alpha-cellulose.

A number of processes have also been put forward in which the cellulose-containing materials are subjected to the action of an oxidising agent, whereby the lignin contained therein is, to a greater or less extent, rendered readily soluble in dilute alkali, and among the oxidising agents which have been proposed are hydrogen peroxide and metal peroxides. However, the use of these agents gives rise to considerable difficulties: indeed hydrogen peroxide, for example, does not by itself oxidise the lignin to any useful extent.

I have now found that the non-cellulosic constituents of woods and other cellulose-containing materials may to a great extent be rendered soluble in dilute alkali by oxidation with peroxides and other oxidising agents providing free oxygen, if the oxidation is carried out in the presence of an organic acid containing in solution a metal salt which is an oxidation catalyst.

According to the invention therefore cellulose-containing materials are subjected to the action of an oxidising agent which acts as a source of free oxygen, or to the action of oxygen itself, in the presence of an organic acid which contains in solution a metal salt which is an oxidation catalyst.

The process is applicable to the treatment of all types of wood, both of a deciduous and non-deciduous character, as well as of other types of cellulosic materials, e.g. straws and grasses. For example, the wood of ash, oak, elm, poplar, birch, beech, larch, pine, spruce

or fir may be treated. Preferably the wood or other material is treated in a finely divided state, for instance in the form of sawdust or small chips. The treatment with the oxidising agent may be assisted, and its consumption reduced, by first treating the cellulosic material with dilute alkali, for example by boiling it with a 1% caustic soda solution. Such boiling may for example be carried out for about an hour.

As the oxidising agent, it is preferred to employ hydrogen peroxide, but other sources of oxygen, for example, metal peroxides, especially alkali and alkaline earth metal peroxides such as sodium peroxide and barium peroxide, may be used, as may free oxygen or air; such other oxidising agents may also be used in association with hydrogen peroxide.

The organic acid used is preferably a lower fatty acid, for example butyric acid, propionic acid and especially acetic acid. Acetic acid, for example, may be used in concentrations of about 25, 50 or 75% or more, concentrations between about 40 and 60% being usually found most satisfactory. The ratio of liquid to cellulosic material may, for example, be 10, 15 or 20 to 1. The amount of oxidising agent necessary will depend to some extent on the nature of the wood or other cellulosic material; for example when hydrogen peroxide is employed proportions of between about 70 and 100 or 120% of the weight of the material are usually required. The reaction temperature may be between about 40° and 70° C. and the treatment may last for about 4 to 6 hours.

As the oxidation catalyst there may be employed a salt of cobalt, nickel, iron, chromium, aluminium and especially of manganese, which is soluble in the reactant medium under the reaction conditions. Preferably a salt of an organic acid is used, and the acetates, especially manganese acetate, have been found to give particularly good results. The amount of catalyst used may for instance be 5, 10 or 15% of the weight of the wood or other cellulose-containing material.

As already indicated the principal effect of the treatment is to oxidise the lignin of the wood or other cellulosic material and to render it soluble in dilute alkali. After the oxidation treatment has been completed, therefore, the cellulosic material may be treated for a short time with a hot dilute solution of alkali to dissolve out the oxidation products; for example it may be boiled with a solution of ½ to 1% sodium hydroxide, and then thoroughly washed. It may then be treated at ordinary temperature with a mercerising solution of 9 to 15% sodium hydroxide in order to remove hemi-celluloses and this treatment may, if required, be repeated several times. In this manner a cellulose having a high alpha-cellulose content and free from substantial quantities of lignin, pentosans and other impurities may be produced. This product may be used for purposes such as paper-making, or it may be converted into viscose, cellulose nitrate or organic esters or ethers of cellulose, e.g. cellulose acetate.

The following example illustrates the invention without in any way limiting it:—

EXAMPLE.

One part of elm sawdust is boiled for about an hour with a 1% solution of sodium hydroxide and then, after washing, is immersed in 12 parts of 45% acetic acid containing 0.8 part of hydrogen peroxide and 0.1 part of manganese acetate. It is heated in this solution for about 4 hours at 70° C. and, after separation from the liquor, boiled for 15 to 30 minutes with ½% solution of sodium hydroxide. Finally, it is mercerised for ½ hour with 8 parts of a 12% solution of sodium hydroxide and treatment repeated until the pentosan content has been reduced to a low figure. The product is then washed and may be employed for the production of cellulose derivatives, for paper-making or for other purposes.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the manufacture of cellulose from cellulose-containing materials, wherein the materials are subjected to the action of an oxidising agent which acts as a source of free oxygen, or to the action of oxygen itself, in the presence of an organic acid which contains in solution a metal salt which is an oxidation catalyst.

2. Process for the manufacture of cellulose from cellulose-containing materials, wherein the materials are subjected to the action of hydrogen peroxide in the presence of an organic acid which contains in solution a metal salt which is an oxidation catalyst.

3. Process according to claim 1 or 2, wherein the treatment is carried out in the presence of a lower fatty acid.

4. Process according to any of the preceding claims, wherein an organic acid salt of manganese, cobalt, nickel, iron, copper or aluminium is employed as catalyst.

5. Process according to any of claims 1 to 3, wherein manganese acetate is employed as catalyst.

6. Process for the manufacture of cellulose from wood, wherein the wood, in the form of chips, sawdust or the like, is subjected at a temperature between 40° and 70° C. to the action of 70—120% of its weight of hydrogen peroxide, in the presence of aqueous acetic acid of 40—60% concentration containing in solution manganese acetate in amount 5—15% of the weight of the wood.

7. Process according to any of the preceding claims wherein, after the treatment with the oxidising agent, the materials are treated with a dilute alkali solution at an elevated temperature.

8. Process according to any of the preceding claims wherein the treatment with the oxidising agent is preceded by treatment with a dilute alkali solution at an elevated temperature.

9. Process for the manufacture of cellulose from cellulose-containing materials substantially as hereinbefore described.

10. Cellulose whenever produced by the process of any of the preceding claims, and cellulose derivatives and other products made therefrom.

Dated this 7th day of January, 1943.

STEPHENS & ALLEN,
Chartered Patent Agents,
Wykeham House,
Gordon Avenue, Stanmore, Middlesex.

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